Modified recycled paper-based adsorbent for nickel removal

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Abstract. The outcome from the industrialization and urbanization promotes the environmental problems especially related to the release of heavy metals. The adsorption method is a promising technique among all the available approaches in heavy metal removal treatment due to its high efficiency, low cost, and simplicity in design and operation. A good selection of solid sorbent becomes one of the greatest problems in adsorption technique. In this present work, we developed recycled paper-based cellulose adsorbent grafted with acrylonitrile in the presence of ceric ammonium nitrate as the initiator. The modified adsorbent was used to adsorb Ni(II) from the aqueous solution. The adsorption process was conducted at different operational conditions by varying the pH of the solution, initial concentration of the Ni(II), and the contact time for the adsorption to reach equilibrium and obtained the highest adsorption capacity. The result demonstrated that the grafted recycled paper-based cellulose adsorbent had improved the adsorption capacity of Ni(II) ions. The most propitious condition obtained was at pH 5 after 1 h, with an initial concentration of 160 mg/L of Ni(II) ions; the removal reached 317.5 mg/g (79.3% removal). The surface studies of the adsorbent before and after Ni(II) ions adsorption was analyzed by using the scanning electron microscopy (SEM). The adsorption equilibrium data of Ni(II) ions was best described by the Freundlich and Pseudo-second-order model. Conclusively, the prepared grafted recycled paper-based cellulose adsorbent proved to be competitive and a promising adsorbent for the removal of Ni(II) ion from aqueous solution, as well as in wastewater treatment application.

1. Introduction

With the diminution of resources sourced from global petroleum and petrochemical, the attraction towards the utilization of renewable and sustainable resources becomes more attractive. Moreover, the urge towards the implementation of renewable-based sources also being triggered due to the serious environmental issue that has been arise day by day. Thus, the approach of the usage of the bio-based materials derived from natural sources was believed can be one of the fascinating strategies for sustainability. Therefore, the development of bio-based materials such as cellulose, chitin, starch and chitosan have been progressively implemented in various fields of industrials [1–4]. Worth to be mentioned that, the most abundant renewable resource that naturally present on earth was

cellulose[5,6]. The cellulose is made up from lots of hydroxyl group with the chemical formula, $(C_6H_{10}O_5)_n$. this organic compound is an unbranched homopolysaccharide with β-D-glucopyranose units connected by (1-4) glycosidic bonds .

Cellulose is a vital component for the green plant since it is the main structural components of the primary cell wall. Due to the nature and the availability of the cellulose, the adaptation of the cellulose-based materials have been well known in many industrials sectors such as electronic device, pharmaceutical and medical materials as well as food packaging [7,8]. However, regarding to the natural sources of the cellulose, it can be produced via two different methods which are top-down process and bottom-up approach [9]. Top-down process involved the production of cellulose-based materials which directly obtained from the plant itself. In conjunction with the top-down process, it gives many advantages especially in terms of environmental safety and ecological disquiet. Meanwhile, the bottom-up approach refers to the extraction of pure cellulose from bacterial fermentation [10,11]. The preparation from this technique can ensure the purity and the uniformity of the extracted cellulose.

Up to present period of time, the employment of the cellulose has still in concern on sustainability. Regarding to this issue, one of the most irresistible sources for the production of pure cellulose was considered on post-consumer recycled paper. Interestingly, it consist high percentage of cellulose, lignin, hemicellulose and other derivative [12–14]. According to Xia et al. [15] the recycled papers contain more than 60 wt% of cellulose. From the frame of reference from waste management, recycled paper was cited as municipal waste and hundred tons of waste recycled papers are annually engendered. In Malaysia, yearly, this municipal waste was produced up to 7,777 tons of paper and paperboard; production of 5,282 tons of pulp for papers; 85, 678 tons of fiber sourced of industrial round woods [16].

Cellulose extracted from recycled papers was successfully implemented as adsorbent. In 2016, Hadi et al. [17] reported on the utilization of the waste newspapers as the cellulose-based adsorbent for the removal of hexavalent chromium with the maximum adsorption capacity up to 59.88 mg/g. Next, the removal of copper was done by using treated newspaper pulp with the optimum removal up to 30 mg/g [18]. Up to the recent updated, the cellulose sourced from recycled paper has shown to be the potential adsorbent. However, in order to optimize the efficiency of the cellulose as the adsorbent, the development of the cellulose has to be modified. Graft copolymerization is a brilliant technique to introduce various kinds of functional group at the cellulose backbones. The grafting process is an attachment of the monomer that is covalently bonded to the main group of the cellulose. The modification alters the physical and chemical properties of the cellulose without affecting the mature properties of the cellulose. Thus far, there is no research on the development of grafted cellulose-based adsorbent sourced from recycled paper. The objective of this research work is to focus on the development of cellulose grafted with acrylonitrile. The grafting process was chemically grafted in the present of ceric ammonium nitrate as the initiator for the creation of active sites on the cellulose backbones. The application of the prepared grafted recycled paper-based adsorbent was used for the removal of nickel (II) from aqueous solution.

2. Experimental

2.1. Materials

For the extraction of cellulose, recycled papers, RPs were included in the printed and unprinted areas. Sodium hydroxide (NaOH) pellets, sodium chlorite ($NaClO_2$) (80 wt%), 65 wt% of nitric acid (HNO_3), and nickel(II) nitrate hexahydrate (N_2NiO_6. $6H_2O$) were received from the Sigma Aldrich. Acrylonitrile monomer, C3H3N and ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$ were purchased from QReC Malaysia. All chemicals were received without any further purification. All solutions were prepared with dilution using distilled water.

2.2 Extraction of cellulose from recycled paper and fabrication of grafted cellulose-based adsorbent

The method for the extraction was done as reported earlier [19]. Extraction of cellulose from recycled papers was accomplished through a process that started from a grinding process to get its fibrous strand. The alkali treatment using 5 wt% of NaOH was applied to RPs for 2 h at 125℃. Subsequently, the bleaching treatment using $NaClO_2$ and a few drops of 60 wt% HNO_3 was executed at 100℃ in duration of 4 h. The process of the bleaching treatment was repeated until the white pulp was obtained. In every repeating step of the bleaching process, the sample was washed with running tap water and distilled water to reach the neutrality of the sample. As the sample reached a pH of 7, the sample was dried in the oven for 24 h at 60℃. Different grafting parameters such as the concentration of the monomer, initiator concentration and grafting reaction were optimized onto the cellulose backbones; the process of the grafting has been discussed in our previous study [19]. The optimized conditions for 1 g of cellulose pulp were acrylonitrile, C_3H_3N = 1.2 g; ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$ = 1.5 g; grafting time = 45 min; and grafting temperature = 70℃. At these optimized grafting condition, both grafting yield, %GY and grafting efficiency, %GE reached 79% and 24%, respectively. After the reaction process, the excess polymer and homopolymer were removed by washing the samples using dimethylformamide (DMF).

2.3 Characterization of the samples

The morphological structure of the adsorbent before and after Ni(II) ions are adsorbed was performed using scanning electron microscopy (SEM) (Hitachi-TM3000 Tabletop Microscope) was utilized. Perkin-Elmer with Model 4100 ZL Atomic Absorption Spectrometer, AAS has been used together with a Perkin-Elmer FIAS-400 flow injection system and an AS-90 autosampler for analysis of final concetration of Ni(II) ions.

2.4 Adsorption study of Ni(II) ions onto grafted-RPs (m-RPs)

Batch experiment was conducted to analyze the performance of the m-RPs as the adsorbent. 1000 mg/L of $N_2NiO_6.6H_2O$ stock solution was prepared. During the adsorption of Ni(II) ions, a fixed adsorbent (0.02 g) was employed in 50-mL stoppered bottles having different concentrations of Ni(II) ions that extended in the range of 40–160 mg/L with a constant pH of 5 for 1 h duration of adsorption time. In the case of kinetic study, the concentration of Ni(II) ions was fixed at 160 mg/L, running at the time range of 0.5 to 6 h, while the other parameters were kept constant. The effect of pH was evaluated by varying the pH from pH 2 to pH 7 with 160 mg/L of Ni(II) ions for 1 h. All of the samples were shaken by using the orbital shaker at a fixed speed of 170 rpm running at room temperature for a definite time. The final concentration of Ni(II) ions was determined by using AAS. The adsorption capacity, q_e and the percentage removal of the adsorption of m-RPs onto Ni(II) ions was calculated using the formula below.

Adsorption capacity, q_e (mg/g) = (Ci-Ce)V/m (1)

Percentage removal (%) = [(Ci-Ce)/Ci] 100% (2)

where;

Ci= Initial concentration of Ni (II) ions (40-160 mg/L) (mg/L)

Cf= Equilibrium concentration reached at definite time (0.5-6 h)(mg/L)

V= Volume of the Ni (II) ions solution during the adsorption test (0.05 L)

m= Weight of the adsorbent used during the adsorption study (0.02 g)

3. Results and discussion

3.1 Morphological structure and elemental analysis

The morphology of the prepared cellulose derived from the RPs and grafted cellulose, m-RPs sample were analyzed by using the scanning electron microscope (SEM). The SEM results that were divulged indicated that the cellulose naturally appeared in fibrous form (Figure 1 a). Meanwhile, the m-RPs showed that the presence of the acrylonitrile monomer had adhered to the fiber on the cellulose, thus changing the physical morphology of the cellulose structure (Figure 1 b). The attachement of Ni(II) ions after adsorption clearly seen in Figure 1(c).

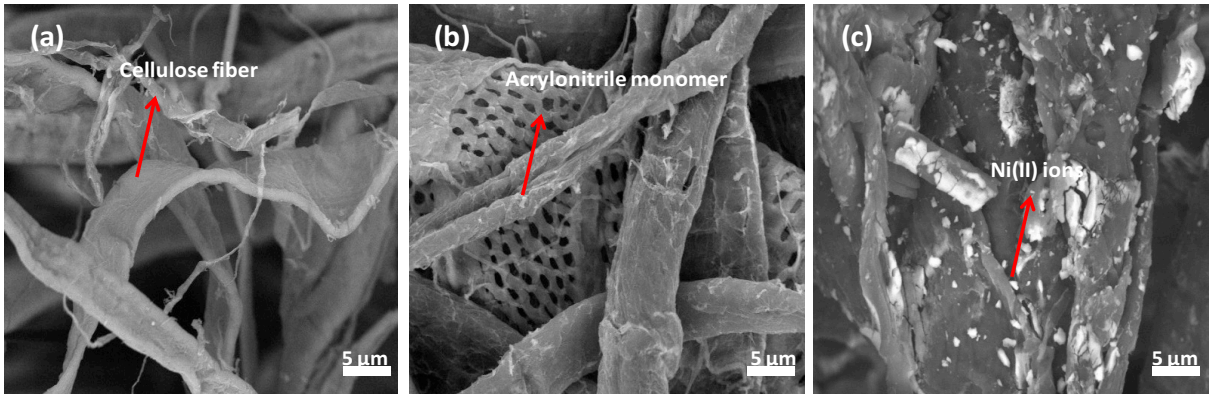

Figure 1. SEM images of (a) RPs (b) m-RPs and (c) m-RPs-Ni.

3.2 Effect of pH of the Ni(II) ions solutions

The pH of the solution containing Ni(II) ions during the adsorption is considered as a major influence that will give a major effect onto the adsorption capacity of the adsorbent. This can be related because of the dissociation of the solution containing hydrogen ions that will compete with the Ni(II) ions. In conjunction with that, the competition between the hydrogen and metal ions can be controlled by the pH of the solution. In the adsorption of the Ni(II) ions, the limitation for the pH of the solution is reached after pH 7. The Ni(II) ions will turn into metal hydroxide, $Ni(OH)_2$; this can clearly be seen due to the appearance of the precipitate in the solution.

In this work, the effect of pH of the solution varies from pH 2 to 7. As the pH of the solution gets higher than pH 5, there is a decrease in the adsorption capacity (Figure 2). This type of trend can be related to the hydrolysis of the Ni(II) ions [20] . At a low pH of between pH 2 to 4, the adsorption performance of m-RPs towards the Ni(II) ions was low. When the pH of the solution nearly reached neutralization, the adsorption of the Ni(II) ions reached its peak. The maximum adsorption capacity obtained at pH 5 had reached 317.5 mg/g, equivalent to 79.3% percentage removal. The process showed that the Ni(II) ions are easily attached to the surface of m-RPs. In addition, it proved that the ions have weak chelating ability towards the adsorbent in an acid condition [1]. Therefore, the adsorption of Ni(II) ions onto m-RPs has to be done in a neutral or nearly-neutral condition, depending on the types of adsorbent.

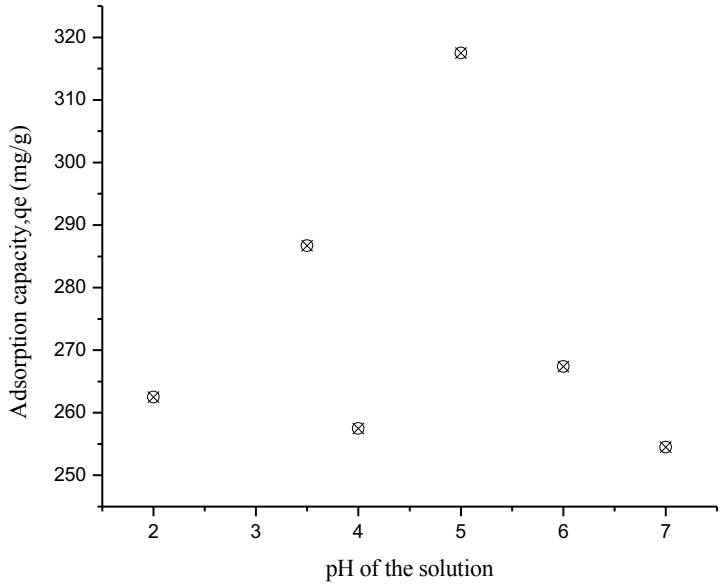

Figure 2. Effect of the pH of the solution of Ni (II) ions onto m-RPs at fixed conditions of contact time= 1h, initial concentration of Ni (II) ions = 160 mg/L with 0.02 g of m-RPs.

3.3 Effect of contact time and kinetic study

Figure 3 plotted the initial Ni(II) ions versus the adsorption capacity of adsorbents that increased as the contact time also increased. The data were plotted with a fixed adsorbent dosage of 0.02 g of 160 mg/L Ni(II) ions at pH 5. The adsorption of Ni(II) ions was measured at different contact times, from 30 min to 6 h, by keeping the other parameters constant. In 1 h, the adsorption capacity of Ni(II) ions onto the m-RPs had increased sharply before slowly decreasing until 6 h. The optimum capacity reached 317.5 mg/g at 1 h of adsorption process with 79.3% of percentage removal. The plots specify that the remaining concentration, which refers to the final concentration of Ni(II) ions, became higher at the time-axis since there was a decrease in the adsorption capacity, even after extending the time for 6 h. As the reaction reached 6 h, the adsorption capacity declined to 287.25 mg/g, equivalent to 69.0% of percentage removal.

There are two models that were used in the adsorption kinetics study: (1) pseudo-first order, and (2) pseudo-second order. These two models applied to resolve for the adsorption mechanism and plausible rate-controlling steps that involve the mass transfer, diffusion control and chemical reaction in the adsorption process. Both of the models can be plotted based on the equations below:

$$\log(qe\text{-}qt) = \log qe - (k1/2.303)t \quad (3)$$

$$t/qt = 1/k2qe2 + t/qe \quad (4)$$

The plottings of log (qe-qt) and t/qt versus t for the first and second model are demonstrated in Figures 4 and 5, respectively. Based on the correlation (R^2), it can be deduced that the pseudo-second-order kinetic model is well fitted to describe the adsorption of Ni(II) ions onto m-RPs.

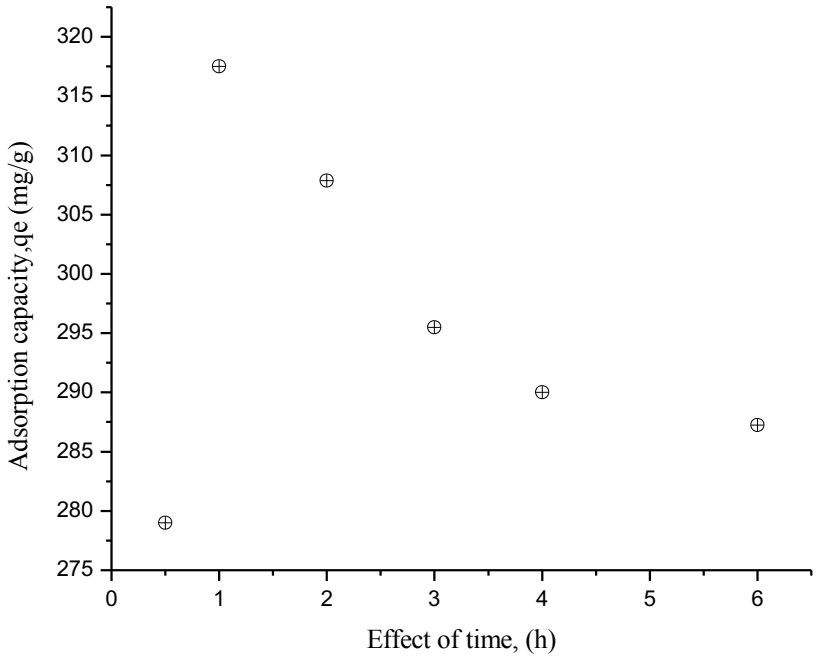

Figure 3. Effect of the contact time of the adsorption of Ni (II) ions onto m-RPs at fixed conditions pH = 5, initial concentration of Ni (II) ions = 160 mg/L with 0.02 g of m-RPs.

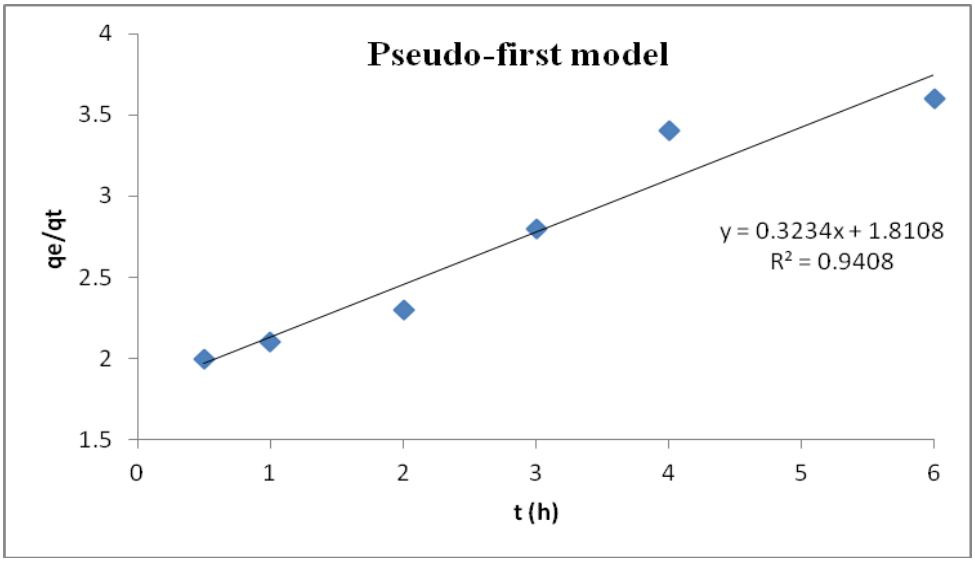

Figure 4. Pseudo-first model of the adsorption of Ni (II) ions onto m-RPs.

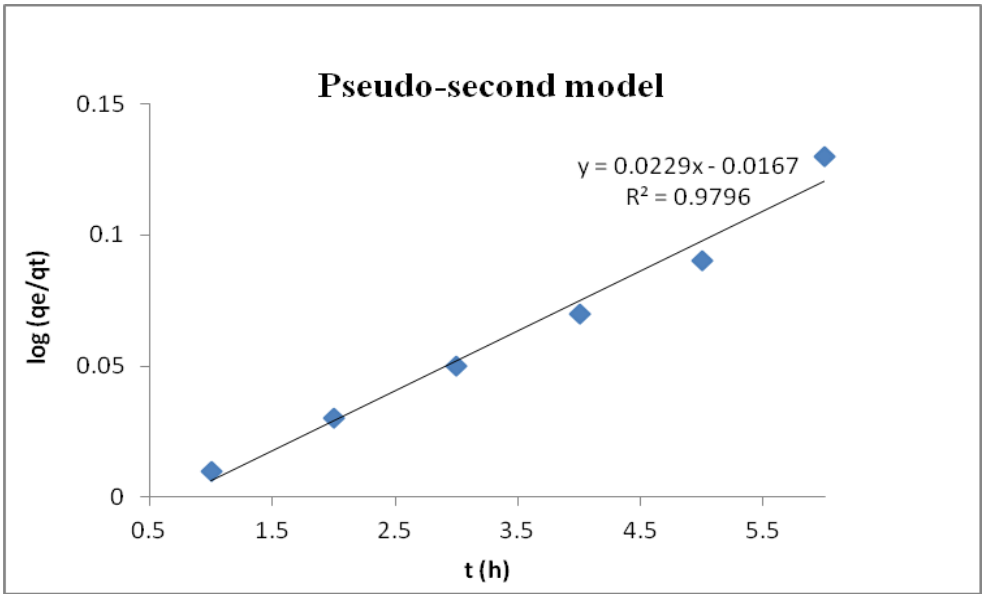

Figure 5 Pseudo-second model of the adsorption of Ni (II) ions onto m-RPs.

3.4 Effect of initial concentration and adsorption isotherms study

In this present work, the effect of the initial concentration of Ni(II) ions was determined as the concentration of the Ni(II) ions that varied in the range of 40 to 160 mg/L. As demonstrated in Figure 6, the adsorption capacity had initially increased and slowly kept increasing up to the concentration of 160 mg/L. The ratio of the moles of Ni(II) ions adsorbed onto the surface of the adsorbent is optimum at the concentration of 160 mg/L, as it recorded the highest adsorption capacity of 212.27 mg/g equivalent to 70.8% of percentage removal. The active site of the adsorbent that became saturated at higher concentrations will lower the diffusion of the metal ions from the solution to the surface of the adsorbent [21].Thus, the removal of Ni(II) ions will keep constant and reach equilibrium. In short, the initial concentration of the Ni(II) ions gives a major effect onto the capability of the adsorption process. As the initial concentration increases, there are more Ni(II) ions that are transported onto the surface of the adsorbent. Thus, this condition will promote the adsorptive quantity that is expressed as the adsorption capacity of the adsorbent.

The adsorption isotherm explains the relationship between the concentrations of the solute in the solution and the amount of the solute adsorbed onto the adsorbent. The study on this isotherm define the metal uptake of the adsorbent by unit mass, q_e to the concentration of the adsorbate at equilibrium, Ce in the running solution. The distribution pattern of the adsorbed metal ions onto the adsorbent can be determined via the adsorption isotherms, which can be generalized into two types of isotherms: Langmuir and Freundlich [22]. The Langmuir isotherm proposed that there is a monolayer adsorption of adsorbate being adsorbed onto the adsorbent's surface. The mathematical formula for the Langmuir model is expressed below:

$$C_e/q_e = (1/q_m)C_e + (1/q_m k_L) \quad (5)$$

where q_e (mg g^{-1}) is refer to the amount of the Ni (II) ions adsorbed per unit mass of m-RPs obtained at equilibrium. Meanwhile, q_m (mg g^{-1}) and k_L (L mg^{-1}) are the Langmuir constants analogous to the maximum adsorption capacity and energy constant of the adsorption capacity, respectively. The relationship of the Langmuir isotherm onto the adsorption process can be obtained by plotting Ce/qe versus Ce. The value of qm and kL can be found from the slope and the intercept from the plotted graph. The Freundlich model proposes that the adsorption between the Ni(II) ions and the m-RPs occurred in the form of multilayer. The model can be obtained by plotting the In q_e against In C_e according to the formulae below:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (6)$$

where K_f and n are Freundlich constants related to adsorption capacity and energy if adsorption respectively. Under the same condition, the adsorption of Ni(II) ions onto the m-RPs for more linear fitting correlation coefficient (R^2) for Langmuir and Freundlich, is 0.7067 and 0.9433, respectively. As demonstrated in Figures 7 and 8, the Freundlich isotherm model obtained a higher R^2 value for the adsorption process using m-RPs. It is demonstrated that the adsorption occurred mainly in the multilayer adsorption.

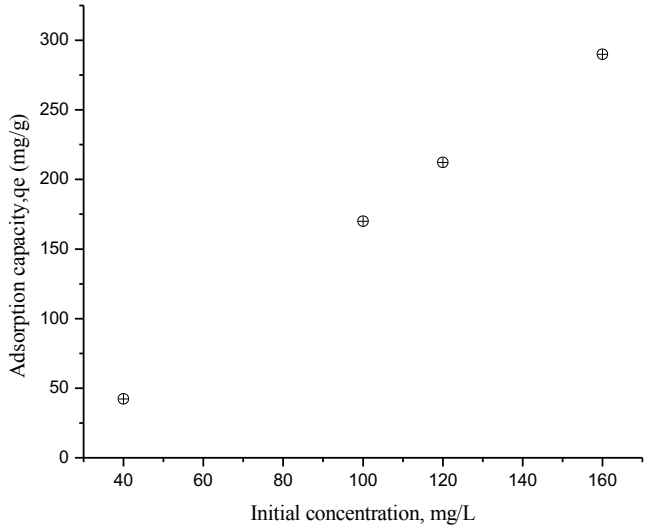

Figure 6 Effect of the initial concentration of Ni (II) ions on the adsorption onto m-RPs at fixed conditions pH = 5, contact time = 1 h with 0.02 g of m-RPs.

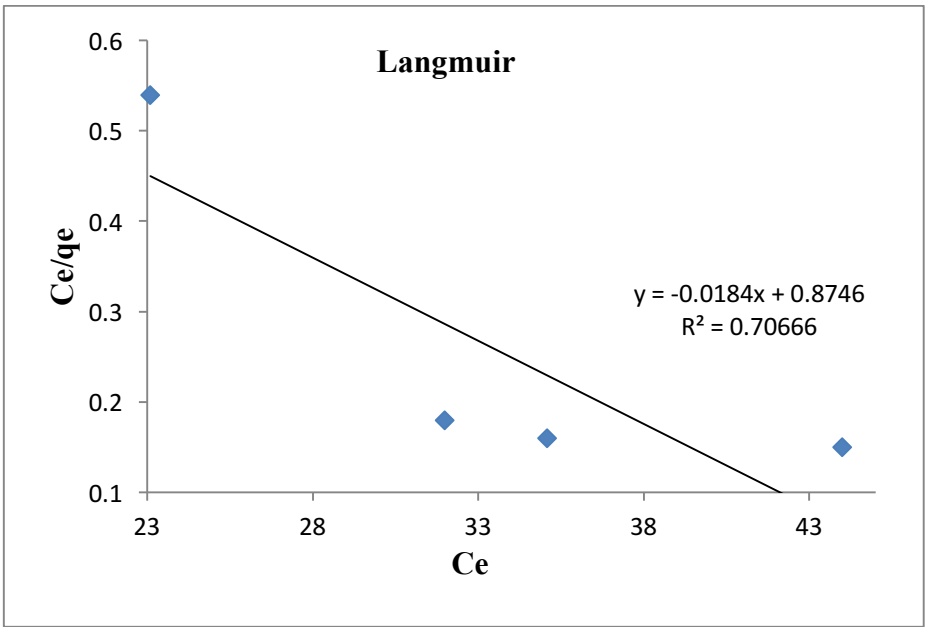

Figure 7 Langmuir model of the adsorption of Ni (II) ions onto m-RPs.

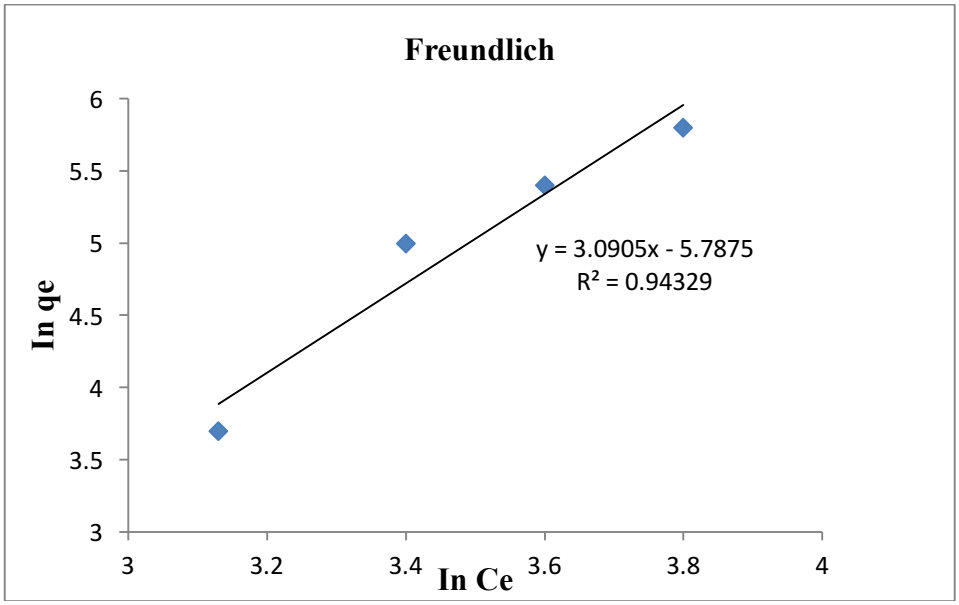

Figure 8. Freundlich model of the adsorption of Ni (II) ions onto m-RPs.

4. Conclusions

Low cost and bioadsorbent from recycled paper was successfully modified with the addition of acrylonitrile using ceric ammonium nitrate via graft copolymerisation process. Chemical treatment of recycled paper with alkali and bleaching agents increase the adsorption capacity. The introduction of additional monomer chain (CH_2=CH-C≡N) during the grafting process to backbone of cellulose can improve the adsorption capacity towards nickel (II) removal as the addition of the monomer enhanced the interaction towards metal ions. The adsorption data was best fitted with Freundlich isotherm model and well described with pseudo-second order kinetic model. The adsorption capacity of grafted recycled paper was comparable to other adsorbent. Thus, it can be used as the alternative adsorbent as a new way to substitute the expensive activated carbon.

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